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| <p>(21) International Application Number: PCT/EP97/02322 (22) International Filing Date: 29 April 1997 (29.04.97) (30) Priority Data: 96201702.6 19 June 1996 (19.06.96) EP (34) Countries for which the regional or international application was filed: AT et al. (71) Applicant (for all designated States except AU BB CA GB IE KE LK LS MN MW NZ SD SG SZ TT UG): UNILEVER N.V. (NL/NL); Weena 455, NL-3013 AL Rotterdam (NL). (71) Applicant (for AU BB CA GB IE KE LK LS MN MW NZ SD SG SZ TT UG only): UNILEVER PLC (GB/GB); Unilever House, Blackfriars, London EC4P 4BQ (GB). (72) Inventors: HERMANT, Roelant, Mathijs; Unilever Research Vlaardingen Lab., Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). JONG, Bas, A., M., J.; Unilever Research Vlaardingen Lab., Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).</p> | | <p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p> |
| <p>(54) Title: BLEACH ACTIVATION (57) Abstract A bleach and oxidation catalyst is provided comprising a catalytically active metal complex having a poly-dentate ligand containing at least 6 hetero atoms. Such metal complexes can activate hydrogen peroxide, peroxy acids or molecular oxygen and were found to have both favourable stain removal and remarkable dye transfer inhibition properties. In addition, these complexes can be easily prepared.</p> | | |

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BLEACH ACTIVATION

Field of the Invention

- The invention relates to activation of bleaches employing
- 5 peroxy compounds including hydrogen peroxide or hydrogen peroxide adducts, which liberate hydrogen peroxide in aqueous solution, peroxy acids or molecular oxygen; to compounds that activate or catalyse peroxy compounds or molecular oxygen; to bleach compositions, including
- 10 detergent bleach compositions, which contain a catalyst for peroxy compounds; and to processes for bleaching and/or washing substrates using the aforementioned types of compositions.
- 15 In particular, the present invention is concerned with the novel use of metal-compounds as catalysts for the bleach activation of peroxy compounds or molecular oxygen.

Background of the Invention.

- 20 Peroxide bleaching agents for the use in laundering have been known for many years. Such agents are effective in removing stains, such as tea, fruit, and wine stains, from clothing at or near boiling temperatures. The efficacy of peroxide bleaching agents drop off sharply at temperatures
- 25 below 60°C.

- Previous patent applications dealt with environmentally acceptable manganese ions and complexes. US patent 4,728,455 discusses the use of Mn(III)-gluconate as
- 30 peroxide bleach catalyst with high hydrolytic and oxidative stability; relatively high ratios of ligand (gluconate) to Mn are, however, needed to obtain the desired catalytic system. Moreover, the performance of these Mn-based catalysts is inadequate when used for bleaching in the low-
- 35 temperature region of about 20°-40°C, and they are restricted in their efficacy to remove a wide range of stains.

In several patent documents, for instance EP-A-458,379, novel triazacyclononane-based manganese complexes are disclosed, which display a high catalytic oxidation activity at low temperatures, which is particularly suitable for bleaching purposes. A major improvement of the bleaching activity could be obtained by the fact that these compounds are stable under washing conditions, e.g. high alkalinity and oxidizing environment (as a result of the presence of hydrogen peroxide or peroxy acids).

In addition to the above-mentioned stain removal, dye transfer is a well-known problem in the art and has been addressed in various ways. For instance, an improved dye transfer inhibition has been obtained by using Fe-porphyrin and Fe-phtalocyanine complexes (see EP-A-537,381, EP-A-553,607, EP-A-538,228).

It is well known that the stability of Fe-co-ordination complexes in alkaline aqueous media in the presence of peroxide compounds is very poor; in EP-A-537,381 and EP-A-553,607, methods are disclosed for improvement in this respect.

This poor stability of Fe-co-ordination species has resulted in the necessity of very low concentrations of peroxide and, additionally, the use of polymers (see EP-A-538,228). These measures, however, only reduce the negative effects of the above-indicated poor stability to some extent and do not provide a complete solution for this problem.

A significant improvement of the stability of iron compounds has been recently obtained by employing pentadentate ligands, thereby providing a high catalytic oxidation activity (see examples WO 95 34628). The synthesis of these complexes and bleaching properties in the presence of H_2O_2 , however, leave room for improvement.

We have now surprisingly found catalytically highly active iron or manganese coordination complexes with polydentate ligands with at least six hetero atoms which can activate dioxygen, hydrogen peroxide or peroxy acids, thereby providing both favourable stain removal and efficient dye-transfer inhibiting properties in the presence of H_2O_2 . In addition these compounds can be easily prepared.

10 Definition of the Invention

In one aspect, the present invention provides a bleach and oxidation catalyst comprising a transition-metal-complex having formula A



or precursors thereof, in which

M is iron or manganese in the II, III, IV, V, VI or VII oxidation state;

- 20 X represents a coordinating species such as H_2O , ROH, NR_3 , RCN, OH^- , OOH^- , RS^- , RO^- , $RCOO^-$, OCN^- , SCN^- , N_3^- , CN^- , F^- , Cl^- , Br^- , I^- , O^{2-} , NO_3^- , NO_2^- , SO_4^{2-} , SO_3^{2-} , PO_4^{3-} or aromatic N donors such as pyridines, pyrazines, pyrazoles, imidazoles, benzimidazoles, pyrimidines, triazoles, thiazoles, with R being H, optionally substituted alkyl, optionally substituted aryl;

1, m, n are integer numbers ranging from 0-3 with $l \leq m$;

Y is a counter ion, the type of which is dependent on the charge of the complex; $q = z/[\text{charge } Y]$;

- 30 z denotes the charge of the complex and is an integer which can be positive, zero or negative; if z is positive, Y is an anion such as F^- , Cl^- , Br^- , I^- , NO_3^- , BPh_4^- , ClO_4^- , BF_4^- , PF_6^- , RSO_3^- , RSO_4^{2-} , SO_4^{2-} , $CF_3SO_3^-$, $RCOO^-$ etc; if z is negative, Y is a common cation such as an alkali metal, alkaline earth metal or (alkyl)ammonium cation etc);

L represents a poly-dentate ligand containing at least six hetero atoms, e.g. N, O, P, S etc.

In another aspect, the present invention provides a bleaching composition comprising a peroxy compound bleach preferably selected from hydrogen peroxide, hydrogen peroxide-liberating or -generating compounds, peroxyacids and their salts, peroxyacid bleach precursors, and mixtures thereof, and a catalyst according to the present invention. Alternatively, a catalyst according to the present invention could be used as such in a formulation, using molecular oxygen as the oxidant.

Detailed Description of the Invention

Generally, the metal-complex catalyst of the invention may be used in a bleaching system comprising a peroxy compound or a precursor thereof or dioxygen and suitable for use in the washing and bleaching of substrates including laundry, dishwashing and hard surface cleaning. Alternatively, the metal-complex oxidation catalyst of the invention may also be used in the textile, fine chemical industries for example for epoxidation or hydroxylation processes, paper and woodpulp industries, or waste water treatment systems.

As already stated, an advantage of the metal-complex catalysts according to the present invention is that they exhibit both a high oxidation activity and a remarkably high stability in alkaline aqueous media in the presence of peroxy compounds.

A second advantage of the metal-complex catalysts of the invention is that the polydentate ligands can be synthetically easily prepared from simple starting materials as shown in the Examples.

An additional advantage is that such compounds are active as dye-transfer inhibition agents in the presence of H_2O_2 , as shown in Example 4.

Another advantage is that the catalysts of the invention have a relatively low molecular weight and are, consequently, very weight-effective.

- 5 Precursors of the active catalysts of the invention can be any metal-co-ordination complex, which, under fabric washing conditions, is transformed into the active metal-complex of general formula A.
- 10 Without wishing to be bound by theory, we postulate that the ligand L coordinates to one or more metal centra in such a way that these metal centra are coordinated by at least five hetero atoms.
- 15 A preferred class of ligands is those that incorporate nitrogens or oxygens as heteroatoms. The nitrogen atoms can be part of tertiary, secondary or primary amine groups, tertiary, secondary or primary amide groups, or part of heterocyclic aromatic ring systems, e.g. pyridines,
- 20 pyrazines, pyrazoles, imidazoles, benzimidazoles, thiazoles, triazoles and pyrimidines, or combinations thereof. The oxygen atoms can be part of carboxylates, alcohols, phenols or phosphonates.
- 25 Examples of preferred ligands in their simplest forms are:
- N,N,N',N'-tetra(pyridin-2-yl-methyl)-ethylenediamine;
N,N,N',N'-tetra(benzimidazol-2-yl-methyl)-ethylenediamine;
N,N,N'-tri(pyridin-2-yl-methyl)-N'-carboxymethyl-
30 ethylenediamine;
N,N,N'-tri(benzimidazol-2-yl-methyl)-N'-carboxymethyl-ethylenediamine;
N,N,N'-tri(pyridin-2-yl-methyl)-N'-hydroxyethyl-ethylenediamine;
35 N,N,N'-tri(benzimidazol-2-yl-methyl)-N'-hydroxyethyl-ethylenediamine;

- N,N'-bis(pyridin-2-yl-methyl)-N,N'-bis(carboxymethyl)
ethylenediamine;
N,N'-bis(benzimidazol-2-yl-methyl)-N,N'-bis(carboxymethyl)
ethylenediamine;
5 N,N'-bis(pyridin-2-yl-methyl)-N,N'-bis(hydroxyethyl)
ethylenediamine;
N,N'-bis(benzimidazol-2-yl-methyl)-N,N'-bis(hydroxyethyl)
ethylenediamine;
N,N,N'-tri(carboxymethyl)-N'-(pyridin-2-yl-methyl)
10 ethylenediamine;
N,N,N'-tri(carboxymethyl)-N'-(benzimidazol-2-yl-methyl)
ethylenediamine;
N,N,N'-tri(hydroxyethyl)-N'-(pyridin-2-yl-methyl)
ethylenediamine;
15 N,N,N'-tri(hydroxyethyl)-N'-(benzimidazol-2-yl-methyl)
ethylenediamine;
1,1,4,8,11,11-hexa(pyridin-2-yl-methyl)-1,4,8,11-tetra-aza-
undecane;
1,1,4,7,7-hexa(pyridin-2-yl-methyl)-1,4,7-tri-aza-heptane;
20 1,7-di(carboxymethyl)-1,4,7-tri(pyridin-2-yl-methyl)-1,4,7-
tri-aza-heptane;
1,7-di(carboxymethyl)-1,4,7-tri(pyridin-2-yl-methyl)-1,4,7-
tri-aza-heptane;
1,4,7-tri(pyridin-2-yl-methyl)-1,4,7-tri-aza-cyclononane;
25 1-(carboxymethyl)-4,7-di(pyridin-2-yl-methyl)-1,4,7-tri-
aza-cyclononane;
1,4-di(carboxymethyl)-7-(pyridin-2-yl-methyl)-1,4,7-tri-
aza-cyclononane;
1,11-di(carboxymethyl)-1,4,8,11-tetra(pyridin-2-yl-methyl)-
30 1,4,8,11-tetra-aza-undecane;
1,11-di(pyridin-2-yl-methyl)-1,4,8,11-tetra(carboxymethyl)-
1,4,8,11-tetra-aza-undecane;

Most preferred ligands are:

N,N,N',N'-tetra(pyridin-2-yl-methyl)ethylenediamine,

hereafter referred to as tpen and

1,1,4,8,11,11-hexa(pyridin-2-yl-methyl)-1,4,8,11-tetra-aza-

undecane, hereafter referred to as hptu.

The metal atom in the catalyst of the present invention is preferably Fe.

- 10 Suitable counter ions are those which give rise to the formation of storage-stable solids. Combination of the preferred iron complexes with the counter ion Y preferably involves counter ions such as RCOO^- , BPh_4^- , ClO_4^- , BF_4^- , PF_6^- , RSO_3^- , SO_4^{2-} , NO_3^- , wherein $\text{R}=\text{H}$, optionally substituted
- 15 phenyl, naphthyl or $\text{C}_1\text{-C}_4$ alkyl. Preferred co-ordinating species X are CH_3CN , H_2O , Cl^- , OH^- , and OOH^- .
- The effective level of the metal-complex catalyst, expressed in terms of parts per million (ppm) of iron in an aqueous bleaching solution, will normally range from 0.001
- 20 ppm to 100 ppm, preferably from 0.01 ppm to 20 ppm, most preferably from 0.1 ppm to 10 ppm. Higher levels may be desired and applied in industrial bleaching processes, such as textile and paper pulp bleaching. The lower range levels are preferably used in domestic laundry operations.

25

The detergent bleach composition

- The bleaching composition of the invention has particular application in detergent formulations to form a new and improved detergent bleach composition within the purview of
- 30 the invention, comprising a peroxy compound bleach as defined above, the aforesaid Fe-complex catalyst having general formula (A), a surface-active material and a detergency builder.
- The Fe-complex catalyst will be present in the detergent
- 35 bleach composition of the invention in amounts so as to provide the required level in the wash liquor. Generally, the Fe-complex catalyst level in the detergent bleach

- composition corresponds to an iron content of from 0.0005% to 0.5% by weight. When the dosage of detergent bleach composition is relatively low, e.g. about 1-2 g/l, the Fe content in the formulation is suitably 0.0025 to 0.5%, preferably 0.005 to 0.25% by weight. At higher product dosages, as used e.g. by European consumers, the Fe-content in the formulation is suitably 0.0005 to 0.1%, preferably 0.001 to 0.05% by weight.
- 10 Detergent bleach compositions of the invention are effective over a wide pH-range of between 6 and 13, with optimal pH-range lying between 7 and 11.

The peroxy bleaching compound

- 15 The peroxy bleaching compound may be a compound which is capable of yielding hydrogen peroxide in aqueous solution. Hydrogen peroxide sources are well known in the art. They include the alkali metal peroxides, organic peroxides such as urea peroxide, and inorganic persalts, such as the
- 20 alkali metal perborates, percarbonates, perphosphates persilicates and persulphates. Mixtures of two or more such compounds may also be suitable.

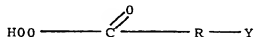
- Particularly preferred are sodium perborate tetrahydrate
- 25 and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because of its high active oxygen content. Sodium percarbonate may also be preferred for environmental reasons. The amount thereof in the composition of the invention usually will be within the
- 30 range of about 5-35 % by weight, preferably from 10-25 % by weight.

- Another suitable hydrogen peroxide generating system is a combination of a C_1 - C_4 alkanol oxidase and a C_1 - C_4 alkanol,
- 35 especially a combination of methanol oxidase (MOX) and ethanol (see Example 3). Such combinations are disclosed in

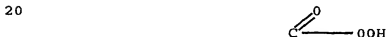
International Application PCT/EP 94/03003 (Unilever), which is incorporated herein by reference.

- Alkylhydroxy peroxides are another class of peroxy bleaching compounds. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

- Organic peroxyacids may also be suitable as the peroxy bleaching compound. Such materials normally have the general formula:



- wherein R is an alkylene or substituted alkylene group containing from 1 to about 20 carbon atoms, optionally having an internal amide linkage; or a phenylene or substituted phenylene group; and Y is hydrogen, halogen, alkyl, aryl, an imido-aromatic or non-aromatic group, a COOH or



group or a quaternary ammonium group.

- Typical monoperoxy acids useful herein include, for example:

- (i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy- α -naphthoic acid;
- (ii) aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, e.g. peroxy lauric acid, peroxy stearic acid and N,N-phthaloylaminoperoxy caproic acid (PAP); and
- (iii) 6-octylamino-6-oxo-peroxyhexanoic acid.

Typical diperoxyacids useful herein include, for example:

- (iv) 1,12-diperoxydodecanedioic acid (DPDA);
- (v) 1,9-diperoxyazelaic acid;
- (vi) diperoxybrassicilic acid; diperoxysebasic acid and diperoxyisophthalic acid;
- 5 (vii) 2-decyldiperoxybutane-1,4-diotic acid; and
- (viii) 4,4'-sulphonylbisperoxybenzoic acid.

Also inorganic peroxyacid compounds are suitable, such as for example potassium monopersulphate (MPS). If organic or
10 inorganic peroxyacids are used as the peroxygen compound, the amount thereof will normally be within the range of about 2-10 % by weight, preferably from 4-8 % by weight.

All these peroxy compounds may be utilized alone or in
15 conjunction with a peroxyacid bleach precursor and/or an organic bleach catalyst not containing a transition metal. Generally, the bleaching composition of the invention can be suitably formulated to contain from 2 to 35% , preferably from 5 to 25% by weight, of the peroxy bleaching
20 agent.

Peroxyacid bleach precursors are known and amply described in literature, such as in the British Patents 836988; 864,798; 907,356; 1,003,310 and 1,519,351; German Patent
25 3,337,921; EP-A-0185522; EP-A-0174132; EP-A-0120591; and US Patents 1,246,339; 3,332,882; 4,128,494; 4,412,934 and 4,675,393.

Another useful class of peroxyacid bleach precursors is
30 that of the cationic i.e. quaternary ammonium substituted peroxyacid precursors as disclosed in US Patent 4,751,015 and 4,397,757, in EP-A0284292 and EP-A-331,229. Examples of peroxyacid bleach precursors of this class are:
2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphonphenyl
35 carbonate chloride - (SPCC);
N-octyl,N,N-dimehyl-N₁₀-carbophenoxy decyl ammonium chloride - (ODC);

3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl
carboxylate; and
N,N,N-trimethyl ammonium toluyloxy benzene sulphonate.

- 5 A further special class of bleach precursors is formed by the cationic nitriles as disclosed in EP-A-303,520 and in European Patent Specification No.'s 458,396 and 464,880.

- Any one of these peroxyacid bleach precursors can be used
10 in the present invention, though some may be more preferred than others.

- Of the above classes of bleach precursors, the preferred classes are the esters, including acyl phenol sulphonates
15 and acyl alkyl phenol sulphonates; the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors including the cationic nitriles.

- Examples of said preferred peroxyacid bleach precursors or
20 activators are sodium-4-benzoyloxy benzene sulphonate (SBOBS); N,N,N'-tetraacetyl ethylene diamine (TAED); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate; SPCC; trimethyl ammonium toluyloxy-benzene sulphonate; sodium nonanoyloxybenzene
25 sulphonate (SNOBS); sodium 3,5,5-trimethyl hexanoyl-oxybenzene sulphonate (STHOBS); and the substituted cationic nitriles.

- The precursors may be used in an amount of up to 12 %, preferably from 2-10 % by weight, of the composition.
30

- As an alternative to the above described peroxide generating systems, molecular oxygen may be used as the oxidant.

35

The surface-active material

The detergent bleach composition according to the present invention generally contains a surface-active material in an amount of from 10 to 50% by weight. Said surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

Typical synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher aryl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher (C_8 - C_{18}) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl (C_8 - C_{18}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10} - C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ester of the higher alcohols derived from tallow or coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher (C_8 - C_{18}) fatty alcohol alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8 - C_{20}) with sodium bisulphite and those derived by reaction paraffins with SO_2 and C_{12} and then hydrolysing with a base to produce a random sulphonate; sodium and ammonium C_7 - C_{12} dialkyl sulphosuccinates; and olefin sulphonates which term is used

- to describe material made by reacting olefins, particularly C_{10} - C_{20} alpha-olefins, with SO_3 and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C_{10} - C_{15}) alkylbenzene sulphonates, sodium C_{16} - C_{18} alkyl ether sulphates.

- Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6 - C_{22}) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxides per molecule; and the condensation products of aliphatic (C_8 - C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-actives include alkyl polyglycosides, sugar esters, long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.
- Amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

- As disclosed by EP-A-544,490, the performance of the hereinbefore described bleach catalyst, may be dependent upon the active detergent system and the builder system present in the detergent bleach composition of the invention.

- The detergent bleach composition of the invention will preferably comprise from 1-15 % wt of anionic surfactant and from 10-40 % by weight of nonionic surfactant. In a

further preferred embodiment the detergent active system is free from C₁₆-C₁₂ fatty acids soaps.

The detergency builder

- 5 The composition of the invention normally and preferably also contains a detergency builder in an amount of from about 5-80 % by weight, preferably from about 10-60 % by weight.
- 10 Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

- Examples of calcium sequestrant builder materials include
- 15 alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic
- 20 acids, citric acid; and polyacetal carboxylates as disclosed in US Patents 4,144,226 and 4,146,495.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

- 25 Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known
- 30 as Zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P type as described in EP-A-0384070.

- In particular, the compositions of the invention may contain any one of the organic and inorganic builder
- 35 materials, though, for environmental reasons, phosphate builders are preferably omitted or only used in very small amounts.

- Typical builders usable in the present invention are , for example, sodium carbonate, calcite/carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyloxy malonate, carboxymethyloxy succinate and
- 5 the water-insoluble crystalline or amorphous aluminosilicate builder material, each of which can be used as the main builder, either alone or in admixture with minor amounts of other builders or polymers as co-builder.
- 10 It is preferred that the composition contains not more than 5% by weight of a carbonate builder, expressed as sodium carbonate, more preferable not more than 2.5 % by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

15

Other ingredients

- Apart from the components already mentioned, the detergent bleach composition of the invention can contain any of the conventional additives in amounts of which such materials
- 20 are normally employed in fabric washing detergent compositions. Examples of these additives include buffers such as carbonates, lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids; lather depressants,
- 25 such as alkyl phosphates and silicones; anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers; stabilizers, such as phosphonic acid derivatives (i.e. Dequest® types); fabric softening agents; inorganic salts and alkaline buffering
- 30 agents, such as sodium sulphate, sodium silicate etc.; and usually in very small amounts, fluorescent agents; perfumes; enzymes, such as proteases, cellulases, lipases, amylases and oxidases; germicides and colourants.
- 35 When using a hydrogenperoxide source, such as sodium perborate or sodium percarbonate, as the bleaching compound, it is preferred that the composition contains not

more than 5 % by weight of a carbonate buffer, expressed as sodium carbonate, more preferable not more than 2.5% by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

5

Of the additives, transition metal sequestrants, such as EDTA and the phosphonic acid derivatives, e.g. ethylene diamine tetra-(methylene phosphonate)-EDTMP- are of special importance, as not only do they improve the stability of the catalyst/H₂O₂ system and sensitive ingredients, such as enzymes, fluorescent agents, perfumes and the like, but also improve the bleach performance, especially at the higher pH region of above 10, particularly at pH 10.5 and above.

15

The invention will now be further illustrated by way of the following non-limiting Examples.

Example 1

- 20 The ligand tpen is easily prepared in one reaction step. 2-Picolyl chloride (31.04 g; 0.19 mol) and ethylenediamine (2.5 ml; 0.04 mol) were heated in 170 ml water in a 250 ml roundbottom-flask to 70 °C. To the resulting clear yellow solution NaOH (33 ml, 10 M) was added dropwise, upon which
- 25 the solution turned dark red. After 66h, solid NaOH (~ 10 pellets) was added until pH >> 11 and the reaction mixture was extracted with CH₂Cl₂, dried with Na₂SO₄ and evaporated to yield 13.7 g of a dark red oil. 7.9 g of this crude product was dissolved in water (4 ml) and perchloric acid
- 30 (40 ml 70-72 %) followed by saturation with ethanol (5 ml). After 1 h a darkbrown precipitate was obtained, which was filtered off, dissolved in (boiled) water and recrystallized. The resulting brown precipitate was dissolved in water (pH > 11) and extracted with CH₂Cl₂. The
- 35 organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated to yield an orange/brown residue consisting of essentially pure tpen (0.24 g, 0.57 mmol) (yield: 3.0 %).

NMR (CDCl_3): ^1H (400MHz) δ (ppm) 2.75 (s, NCH_2 , 4H), 3.76 (s, pyridylmethyl CH_2 , 8H), 7.08 (t, pyridine H, 4H), 7.42 (d, pyridine H, 4H), 7.54 (t, pyridine H, 4H), 8.46 (d, pyridine H, 4H).

5 IR (cm^{-1}) (KBr): 3012 (m), 2952 (m), 1590 (s), 1566 (s), 1474 (s), 1437 (s), 1367 (m), 1357 (m), 1312 (m), 1240 (m), 1121 (m), 1104 (m), 1097 (m), 997 (m), 973 (m), 961 (m), 897 (m), 774 (s), 761 (s).

Melting point: 107.7 - 109.9 °C

10 MS (MeOH) (scan range 100-1000 m/z): 425 $[\text{M} + \text{H}]^+$

Preparation of $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2$.

tpen (0.81 g; 1.91 mmol) was dissolved in argon degassed methanol (35 ml). Under vigorous stirring, $\text{Fe}(\text{II})(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$

15 (0.69 g; 1.91 mmol) in 20 ml degassed MeOH was added dropwise upon which the solution turned red/brownish. After stirring for another 3 minutes, the solution was left for three days to yield red/brownish crystals of $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2$ which were washed with icecold ethanol and diethylether. Yield: 0.92 g, 1.35 mmol (71%).

^1H -NMR (D_2O): δ (ppm) 6.50 (br. s), 7.94 (s), 9.17 (s), 9.68 (br. s), 12.32 (br. s)

IR (cm^{-1}) (KBr): 3441 (s), 3060 (w), 2925 (w), 2889 (w), 1089 (s)

25 Anal. Found (Calcd for $\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{FeN}_6\text{O}_8$): C, 46.13(45.97); H, 4.15(4.15); N, 12.2(12.37); O, 18.5(18.84); Cl, 11.1(10.44); Fe, 8.04(8.22).

In the Examples, the above-described complex

30 $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2$ is referred to as $\text{Fe}(\text{tpen})$.

Example 2

The ligand hptu is easily prepared in one reaction step.

2-Picolyl-chloride (14.06 g, 85.7 mmol) and N,N'-bis(2-aminoethyl)-1,3-propanediamine (2 g, 12.5 mmol) were
35 dissolved in water (70 ml) and heated to 70 °C. NaOH (17 ml, 10 N) was added dropwise in a time span of 45 minutes

after which the mixture was stirred for another 1.5 hours at 70 °C. After cooling to room temperature, the mixture was extracted with dichloromethane which was evaporated to leave a reddish oil (9.36 g) which consisted of essentially pur hptu.

¹H-NMR (CDCl₃) δ (ppm): 8.47-8.48 (m, 4H), 8.44-8.45 (m, 2H), 7.55-7.59 (m, 4H), 7.47-7.51 (m, 2H), 7.43-7.45 (d, 4H), 7.26-7.28 (d, 2H), 7.05-7.10 (m, 6H), 3.78 (s, 8H), 3.62 (s, 4H), 2.64 (s, 8H), 2.36 (t, 4H), 1.57-1.53 (m, 2H)
MS: 707 [M+H]⁺

Preparation of [Fe₂(hptu)(CH₃CN)₂](ClO₄)₄.

The ligand hptu (0.5 g, 0.7 mmol) was dissolved in 4 ml MeOH and 1 ml H₂O. Fe(III)(ClO₄)₃·6H₂O (0.65g, 1.4 mmol) was added under stirring upon which an orange-brown solid precipitated. The precipitate was recrystallized from MeOH/H₂O (2.5:1) to yield 70 mg of an orange-brown crystalline solid, ascribed to [Fe₂(hptu)(OH)₂](ClO₄)₄.

¹H-NMR (D₂O): δ (ppm) -10 (br.s); 0 (br.s); 2-20 (m); 78 (br.s); 88 (br.s); and 103 (br.s).

IR (cm⁻¹) (KBr): 3426 (m), 1609 (m), 1090 (s), 770 (w), 623 (m).

In the Examples, the above-described complex is referred to as Fe₂(hptu).

Example 3

The bleaching activity of the Fe-catalysts prepared according to Example 1 and 2 were demonstrated in the presence hydrogen peroxide on standard tea-stained (BC-1) cotton test cloths.

The experiments were carried out at 40°C and at a pH of 7, 8.5 and 10 in a temperature-controlled glass beaker equipped with a magnetic stirrer, thermocouple and a pH electrode.

Two pieces of test cloth were stirred for 30 minutes in 100 ml of ca 8.3×10^{-3} mol/l hydrogen peroxide solution in millipore water, containing concentrations of the compounds as indicated in Table 1. After rinsing with demineralised water, the test cloths were dried for 7 minutes in a microwave oven. The reflectance (R_{460}^*) of the test cloths was measured on a Macbeth 1500/plus colour measuring system including UV-filter before and after treatment. The difference (ΔR_{460}^*) between both reflectance values thus obtained gives a measure of the bleaching performance, i.e. higher ΔR_{460}^* values correspond to an improved bleaching performance.

TABLE 1

| 15 | conc. | ΔR_{460}^* | ΔR_{460}^* | ΔR_{460}^* |
|------------------------|---------------------|--------------------|--------------------|--------------------|
| | (mol/l) | pH=7 | pH=8.5 | pH 10 |
| blank | - | 2.5 | 3.3 | 7.0 |
| Fe(tpen) | 10×10^{-6} | 7.4 | 10.3 | 9.9 |
| Fe ₂ (hptu) | 5×10^{-6} | 6.3 | 11.3 | 12.6 |

20

In Table 1, Fe(tpen) and Fe(hptu) refer to the Fe-catalysts prepared according to Example 1 and 2. The blank experiments were used as control.

25 These measurements show that improved bleaching performance is obtained when Fe(tpen) or Fe₂(hptu) are present in solution.

30

Example 4

35 The dye oxidation activity of the Fe-catalysts prepared according to Example 1 and 2 was demonstrated in the presence of hydrogen peroxide on the dye acid red 88.

The experiments were carried out at 40 °C at pH = 4, 7, 8.5 and 10 in a 1 cm cuvet in the presence of 8.9×10^{-3} mol/l hydrogen peroxide and 60×10^{-6} mol/l acid red 88. The absorbance at 500 nm (A_{500}), which is the maximum of the characteristic visible absorption of the dye in aqueous media, was measured at $t=0$ ($A_{500}^{t=0}$) and $t=30$ minutes ($A_{500}^{t=30}$). The ratio ΔA_{500} ($= 100 \times (A_{500}^{t=0} - A_{500}^{t=30}) / A_{500}^{t=0}$) represents the percentage dye oxidized and gives a measure of the dye-transfer inhibition performance, i.e. an improved dye-transfer inhibition results in increased ΔA_{500} values.

TABLE 2

| | conc. (mol/l) | ΔA_{500} pH=4 | ΔA_{500} pH=7 | ΔA_{500} pH=8.5 | ΔA_{500} pH=10 |
|------------------------|---------------------|--------------------------|--------------------------|----------------------------|---------------------------|
| | | | | | |
| blank | | 2 | 0 | 0 | 8 |
| Fe(tpen) | 10×10^{-6} | 81 | 70 | 62 | 51 |
| Fe ₂ (hptu) | 5×10^{-6} | 74 | 67 | 44 | 22 |

In Table 3, Fe(tpen) and Fe₂(hptu) refer to the Fe-catalysts prepared according to Example 1 and 2. The blank experiments were used as control.

These measurements show that improved dye oxidation performance is obtained when Fe(tpen) or Fe₂(hptu) is present in solution.

CLAIMS

1. a bleach and oxidation catalyst comprising a transition-metal-complex having formula A



or precursors thereof, in which

M is iron or manganese in the II, III, IV, V, VI or VII oxidation state;

X represents a coordinating species such as H_2O , ROH, NR_3 , RCN, OH^- , OOH^- , RS^- , RO^- , $RCOO^-$, OCN^- , SCN^- , N_3^- , CN^- , F^- , Cl^- , Br^- , I^- , O^{2-} , NO_3^- , NO_2^- , SO_4^{2-} , SO_3^{2-} , PO_4^{3-} or aromatic N donors such as pyridines, pyrazines, pyrazoles, imidazoles, benzimidazoles, pyrimidines, triazoles, thiazoles, with R being H, optionally substituted alkyl, optionally substituted aryl;

l, m, n are integer numbers ranging from 0-3 with $l \leq m$;

Y is a counter ion, the type of which is dependent on the charge of the complex; $q = z / [\text{charge } Y]$;

z denotes the charge of the complex and is an integer which can be positive, zero or negative; if z is positive, Y is an anion such as F^- , Cl^- , Br^- , I^- , NO_3^- , BPh_4^- , ClO_4^- , BF_4^- , PF_6^- , RSO_3^- , RSO_4^- , SO_4^{2-} , $CF_3SO_3^-$, $RCOO^-$ etc; if z is negative, Y is a common cation such as an alkali metal, alkaline earth metal or (alkyl)ammonium cation etc);

L represents a poly-dentate ligand containing at least six hetero atoms, e.g. N, O, P, S etc..

2. Catalyst according to Claim 1, wherein L coordinates to one or more metal centra in such a way that these metal centra are coordinated by at least five hetero atoms.

3. Catalyst according to Claim 2, wherein the hetero atoms are selected from nitrogen or oxygen atoms.

4. Catalyst according to any of Claims 1-3, wherein X represent co-ordinating species selected from CH_3CN , H_2O , Cl^- , OH^- , O_2^{2-} or OOH^- .
5. Catalyst according to any of Claims 1-4, wherein the counter ion Y is selected from RCOO^- , BPh_4^- , ClO_4^- , BF_4^- , PF_6^- , RSO_3^- , RSO_4^- , SO_4^{2-} , NO_3^- , wherein R=H, optionally substituted phenyl, naphthyl or $\text{C}_1\text{-C}_4$ alkyl.
6. Catalyst according to any of Claims 1-5, wherein the ligand L is N,N,N',N'-tetra(pyridin-2-yl-methyl)ethylenediamine or hexa(pyridin-2-yl-methyl)-1,4,8,11-tetra-aza-undecane.
7. A catalytic oxidation system comprising a catalyst according to any of the preceding claims 1-6 and dioxygen, hydrogen peroxide, peroxy acids, hydrogen-peroxide generating systems or bleaching activators.
8. A bleaching composition comprising a peroxy bleaching compound and a catalyst according to any of the preceding claims 1-6.
9. Composition according to claim 8, which comprises said peroxy bleaching compound at a level of from 2 to 35% by weight and said catalyst at a level corresponding to an iron content of from 0.0005 to 0.5% by weight.
10. Composition according to claim 8 or 9, wherein the peroxy bleaching compound is selected from the group consisting of hydrogen peroxide, hydrogen peroxide-liberating or -generating compounds, peroxyacids and their salts, peroxyacid bleach precursors, and mixtures thereof.
11. Composition according to any of claims 8-10, which further comprises a surface-active material, in an amount

of from 10 to 50% by weight, and a detergency builder in an amount of from 5 to 80% by weight.

INTERNATIONAL SEARCH REPORT

Inter national Application No
PCT/EP 97/02322

| A. CLASSIFICATION OF SUBJECT MATTER | | |
|---|---|--|
| IPC 6 | C1103/39 | B01J31/18 C07F15/02 C07F13/00 |
| According to International Patent Classification (IPC) or to both national classification and IPC | | |
| B. FIELDS SEARCHED | | |
| Minimum documentation searched (classification system followed by classification symbols) | | |
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| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
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| * Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family | | |
| Date of the actual completion of the international search | | Date of mailing of the international search report |
| 27 October 1997 | | 06.11.97 |
| Name and mailing address of the ISA European Patent Office, P.B. 5816 Patentstein 2 NL - 2280 HV Rijswijk Tel: (+31-70) 340-2040, Tx: 31 651 epo nl, Fax: (+31-70) 340-3016 | | Authorized officer Grittern, A |

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